

Effect of Organic and Inorganic Additives in Membrane Composition on the Properties and Performance of Nanofiltration Membrane for Xylose and Glucose Separation

NUR'AMIRAH BINTI ABDUL GHAFAR

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**Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG**

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ABSTRACT

World production of biomass is estimated at 146 billion tons a year. The biomass resources can be used to meet variety of needs such as energy needs and food industries. Xylose and glucose are among the most abundant component that can be found in the biomass source. The purpose of the separation of xylose from glucose is to fully utilize the sugar component from the biomass source. Recent studies have found that nanofiltration (NF) method is possible for separation of xylose and glucose. Compared to the chromatography process, NF membrane is simple process, cost-effective and easy-maintenance. The objective of this study is to study the effect of organic and inorganic additives in membrane composition on the properties and performance of NF membrane for xylose and glucose separation. PES polymer is used in a casting solution with N-Methyl-2-pyrrolidone (NMP) as a solvent, PEG-200 and zinc chloride (ZnCl_2) as an additive to the solution. The membrane performance of the membrane is investigated by varying 2 different types of additives with concentration that is 2 wt. %, for PEG-200 and 2 wt. % for zinc chloride. Membrane performance test was carried out with dead end filtration test by using Amicon Millipore stirred cell (Model 8200) with constant stirring speed at 300 rpm and temperature at ambient. Refractometer was used to analyse the samples concentration from separation process. It is found from the developed membrane, the addition of additives shows decreases in flux and the membrane permeability. The membrane type also changes from NF to RO range as organic additives and inorganic additives are mixed together. The membranes also have 99% rejection for both xylose and glucose and separation factor of xylose from glucose is almost 1. From the separation factor it shows that the membrane cannot separate the xylose from glucose. From the pore radius calculation it is found that the membrane pore size is in average 0.3 nm for all membrane had become one of the reason xylose cannot separated as its radius bigger than the pore size and xylose cannot pass through the membrane.

Key words: Biomass, Nanofiltration membrane, Separation Xylose/Glucose, Organic Additives, Inorganic Additives

ABSTRAK

Di seluruh dunia, bahan biomas dihasilkan dianggarkan berjumlah 146 juta bilion tan setiap tahun. Sumber bahan biomas boleh digunakan untuk menepati pelbagai keperluan seperti sumber tenaga dan di dalam industry makanan. Xylose dan glukosa adalah komponent paling banyak yang boleh dijumpai di dalam sumber biomas. Tujuan memisahkan xylose daripada glukosa adalah untuk menggunakan sepenuhnya komponen gula yang terdapat di dalam sumber biomas. Kajian terbaru telah menemui membran nanofiltrasi mampu untuk memisahkan xylose dan glukosa. Berbanding dengan process kromatografi, membrane nanofiltrasi adalah lebih mudah, kos efektif dan mudah untuk diselenggara. Tujuan kajian ini adalah untuk mengkaji kesan penambahan bahan tambahan organik dan bukan organik di dalam komposisi membrane terhadap sifat and prestasi NF membran untuk pemisahan xylose dan glukosa. PES polimer digunakan di dalam larutan bersama N-Methyl-2-pyrrolidone (NMP) sebagai pelarut, PEG-200 dan zink klorida $ZnCl_2$ sebagai tambahan kepada larutan. Prestasi membrane diuji dengan menggunakan berlainan jenis bahan tambahan dengan kepekatan 2 % berat untuk PEG-200 dan 2 wt. % untuk zink klorida. Untuk ujian prestasi membrane dijalankan menggunakan penapisan ujian buntu menggunakan Amicon Millipore sel dikacau (Model 8200) dengan kelajuan tetap pada 300 putaran per minit dan suhu ambien. Refractometer digunakan untuk menguji kepekatan sampel yang diambil dari ujian buntu. Hasil daripada kajian mendapati penambahan bahan tambah menunjukkan penurunan dalam fluks dan kebolehtelapan membran. Jenis membran juga berubah dari NF kepada RO apabila bahan tambah organik dan bahan tambah bukan organik dicampur sekali. Membran yang dihasilkan juga menunjukkan 99% penolakan terhadap xylose dan glukosa dan faktor pemisahan xylose daripada glukosa hampir 1. Daripada faktor pemisahan itu menunjukkan membran yang dihasilkan tidak dapat memisahkan xylose daripada glukosa. Pengiraan radius liang membrane menunjukkan purata saiz adalah 0.3nm untuk kesemua membrane antara satu sebab xylose tidak dapat dipisahkan kerana radius molekul xylose lebih besar daripada liang membran.

Kata kunci: Biomass, Nanofiltration membran, Pemisahan Xylose/Glukosa, Bahan tambah Organik, Bahan tambah bukan organik

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LIST OF SYMBOLS

R_{xyl}	retention of xylose
R_{glu}	retention of glucose
X_{xyl}	xylose separation factor

Subscripts

f	feed
p	permeate
c	concentrate
r	retentate

LIST OF ABBREVIATIONS

PES	Polyethersulfone
NMP	N,N-dimethylformamide
PEG-200	Polyethylene Glycol (200)
NF	Nanofiltration
UF	Ultrafiltration
MF	Microfiltration
RO	Reverse Osmosis
MWCO	Molecular weight cut off

1 INTRODUCTION

1.1 Background of study

Biomass is organic substances mainly composed of carbon, hydrogen and oxygen. They are living or have recently lived in the world and have solar energy stored in its molecular bonds. The resources included wood and wood wastes, agricultural crops and their waste byproducts, municipal solid waste, animal wastes, waste from food processing, aquatic plants and algae. Biomass consists of any heterogeneous mixture of organic substances and a small amount of inorganic substances (Demirbas, 2001). Biomass could be the source of lignocellulose feedstock as they have high carbohydrate content and have potential for large-scale bioethanol production. Lignocellulose consists of lignin, carbohydrates such as cellulose and hemicellulose, pectin, proteins, ash, salt and minerals (Van Dyk and Pletschke, 2012). Cellulose is the predominant polymer in lignocellulosic biomass and can be converted to ethanol in a two-step process. First process is through hydrolysis to convert cellulose to glucose sugar and then converted to ethanol by fermentation process (El-Zawawy et al., 2011).

Most of the monosaccharides such as glucose and xylose are very important for the ingredients in food, pharmaceutical industries and as a source of alternative energy. The pure fractions of a specific monosaccharides are thus needed for the production of xylitol and ethanol but the separation of monosaccharides from each other is quite complex for the industrial scale (Sjoman et al., 2007). The separation is important for the commercial purification of xylose for xylitol production. The uses of xylitol in the food industry keep on increasing because of their several advantages such as anticarcinogenic properties, does not cause acid formation, and having low viscosity and negative heat effect when dissolved in a solution.

Currently, the common method used to separate xylose from glucose is by using liquid chromatography. Chromatography is very efficient method to separate chemical compound (Bi et al., 2010) but sometimes it can involve very complex step. A more cost-effective and easy maintenance technique for sugar separation using nanofiltration (NF) membrane was showed by (Sjoman et al., 2007). However, they are using commercial NF membrane.

In the current study, flat sheet NF membrane was developed to separate xylose from glucose. Polyethersulfone (PES) was used as a polymer material with N-Methyl-2-pyrrolidone (NMP) as a solvent. The effect of organic additives, Polyethylene glycol (PEG-200) and inorganic additives, zinc chloride on the membrane performance was studied.

1.2 Motivation

The current method available in the industry to recover xylose is chromatographic separation. While for separation of xylose from glucose by using nanofiltration membrane, currently there is no commercial membrane that is specifically design for sugar separation. During the membrane preparation, some of the crucial factors that need to be controlled are the amount and type of polymer used, type of solvent and additives added into the spinning dope solution (Feng et al., 2013). The blending/additives technique has been considered to be one of the methods for surface improvement of membrane such as hydrophilicity, surface roughness, surface charge, and the pore size (Ahmad et al., 2013). The additives presence in the membrane solution will influence thermodynamic and kinetic properties of membrane solution. It will reduce the strength of polymer-solvent interaction and increase solvent-non solvent exchange rate to enhance the precipitation rate of membrane. By varying the additive concentration and molecular weight, enlarged or suppressed macrovoid can be obtained (Teta et al., 2013). The effect of different PEG molecular weight to PES in the casting solution already being studied on membrane morphologies and permeation properties by Idris et al., (2007). Currently none of the study on the effect of additives focuses on the separation of xylose and glucose.

1.3 Objective of the research

The objective of this research is to study the effect of organic and inorganic additives in membrane composition on the properties and performance of NF membrane for xylose and glucose separation.

1.4 Scopes of this research

The following scopes of research were outline in order to achieve the research objectives:

- i. To cast flat sheet membrane through casting method using 18 wt. % polyethersulfone (PES) in different amount of additives dissolves in N-Methyl-2-pyrrolidone (NMP) solvent
- ii. To study the effect of two different additives composition of PEG 200 (2 wt.%) and ZnCl_2 (2wt.%) in PES dope polymer solution
- iii. To characterize the properties of NF membrane in terms of water flux and pore size.
- iv. To evaluate the performance of NF in terms of retention and separation factor for xylose/glucose under dead end filtration.

1.5 Main contribution of this work

The following are the contributions of this study:

- a) The best type of additives that give better morphology, water flux and membrane pore size to be used for xylose and glucose separation.
- b) The effectiveness of using 2 different additives in the same dope solution for better retention of glucose and separation factor for xylose and glucose separation.
- c) This work will add more research being done to improve the membrane performance for better separation of xylose from glucose.

1.6 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides the literature review for this study. It started with the introduction of biomass where it generally describes the source of biomass and the advantages of utilizing biomass source. This chapter continues to introduce the process involved in biomass processing. Different conversion technologies of biomass are explained briefly. After that, sugar separation technology are being introduces. Currently, there are two methods to separate sugar that is chromatography that already being used commercially and then by using nanofiltration membrane that still in research scale. Membrane technology was discussed next in the literature review which covered

different types of membrane technology such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis. For the separation of xylose from glucose, the best type of membrane process is by using nanofiltration as it has higher selectivity than ultrafiltration and microfiltration membrane and lower pressure needed than reverse osmosis. This chapter continues with the explanation about nanofiltration membrane (NF) and then the effect of additives on the membrane formation.

Chapter 3 describes the material and methodology used in this study. The chapter started with an overview of the whole methods involve follow by brief introduction about the chapter. The following part was covered in Chapter 3 such as, chemicals being used, membrane fabrication method, dead end filtration and analytical method for sugar analysis.

Result and discussion were discussed in the Chapter 4. This followed by the last chapter, which is Chapter 5 that draws the conclusion from current study and lists several recommendation for future study.

2 LITERATURE REVIEW

2.1 Biomass

Biomass is the name given to all the earth's living matter. Its resources come from wood, wood wastes, agricultural crops and their by-products, municipal solid wastes, animal wastes, waste from food processing, aquatic plants and algae. The classification of biomass according to its origin is shown in Figure 2-1 (Roberts et al., 2015). It is an organic substance that is mainly composed of carbon, hydrogen and oxygen (Tekin et al., 2014). World production of biomass is estimated at 146 billion tons a year and most of it is wild plant growth. The biomass resources can be used to meet a variety of energy needs, including generating electricity, heating homes, fueling vehicles and providing process heat for industrial facilities (Demirbas, 2001). The energy in biomass from plant matter originally comes from solar energy through the photosynthesis process. It will be stored in plants and animals and recovered by burning biomass as fuel (Demirbas, 2001).

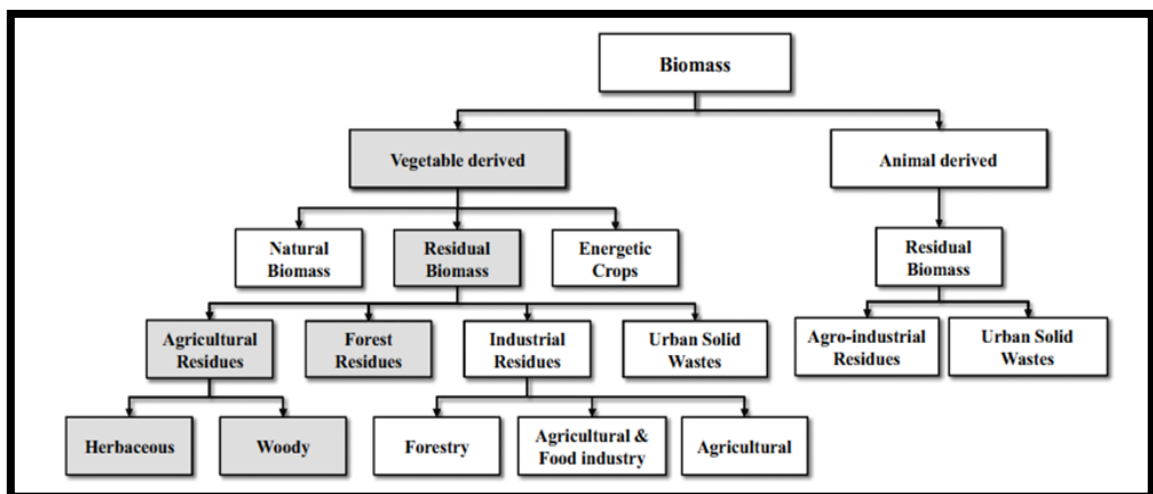


Figure 2-1 Classification of biomass according to its origin (Roberts et al., 2015).

As a result of increasing world population and rapidly evolving industries, energy demand constantly increasing. The consumption of fossil fuels such as oil, coal and natural gas had increased and caused significant environmental pollution. Harmful gases linked to the greenhouse effect and global warming, have been released into the atmosphere. These phenomena had made the search for alternative energy sources have gained great importance because uses of fossil fuels are harmful to the environment and their supply also is limited (Tekin et al., 2014). Besides that, the point where the cost of

producing energy from fossil fuels exceeds the cost of biomass fuels has been reached making the use of biomass as renewable energy keep on increasing (Demirbas, 2001).

Biomass has high utilization potential as an alternative to fossil fuels and one of the most important energy sources of the future. The advantage of biomass is that it is a clean energy source as the usage of this energy does not add carbon dioxide to the environment. The carbon dioxide taken from the atmosphere by plants through photosynthesis is utilized by the plants as a source of energy and returned to the atmosphere without additional carbon dioxide released (Tekin et al., 2014). By using biomass as a source of energy and replacement of non-renewable energy source could result in net reduction in greenhouse gas emissions as it is carbon dioxide neutral. Besides that, biomass fuels have negligible sulphur content which does not contribute to sulphur dioxide emission that cause acid rain.

In addition, biomass is known as the most common forms of renewable energy (Mckendry, 2002). The formation of fossil fuels takes millions of years, while plants used as a source of biomass that grow in periods of months or years. Among the renewable energy resources, biomass has a high utilization potential among renewable energy resources. It can be directly burn or indirectly by converting it into liquid or gaseous fuel.

Besides that, uses of biomass from wastes can give good influence to the economics of plant operations and also helps to solve problem on disposal of wastes in the developed country. One analysis provided by the United Nations Conference on Environment and Development estimates that biomass could supply about half of the present world primary energy consumption by the year 2050.

Biomass source is a potentially sustainable and relatively environmentally benign source of energy. Using of biomass resources also could reduce the problems towards waste disposal. As for the benefits of using biomass energy it will provide clean, renewable energy source that could dramatically improves our environment, economy and energy security. Other than that, biomass energy will generate far less air emissions than fossil fuels, reduces the amount of waste sent to landfills and decreases our reliance on foreign oil.

In addition, production and utilization of bioethanol had attracted a worldwide attention as a strategy for reducing global warming and to improve global energy security. Since 2007, most of the bioethanol produced from sugar or a starch that is obtained from fruits and grains. Ethanol also could be produced from a number of renewable resources other than starches or sugar such as lignocellulosic materials. Currently, lignocellulosic materials continue to be investigated as a source of fermentable sugars for biofuels production because of its high availability (Tekin et al., 2014).

2.2 *Biomass processing*

A biomass is any heterogeneous mixture of organic substance and a small amount of inorganic substance. Cellulose, hemicellulose, lignin, and extractives are the main components of lignocellulosic materials. Lignocellulose feed stock, such as agricultural and forest residues, industrial and municipal wastes, and dedicated energy crops, by virtue of their high carbohydrate content, hold tremendous potential for large-scale bioethanol production. Lignocellulosic waste materials contain cellulose that is the predominant polymer in combination with lignin and hemicellulose in smaller amount. The cellulose compound can be converted into glucose sugar by hydrolysis and the resulting sugars can be converted to ethanol by fermentation. There also has been significant progress in the conversion of vegetable oil and animal fat into biodiesel as an alternative to petroleum-based diesel fuels. Biodiesel can be produced by the transesterification of oils. Oils obtained from plants, such as soybean, canola, corn, and rapeseed, are the most widely used raw materials for biodiesel production (Tekin et al., 2014).

Technologies used to convert biomass into either bio-fuel with high energy content or valuable chemicals can be classified under two groups as shown in the Figure 2-2.

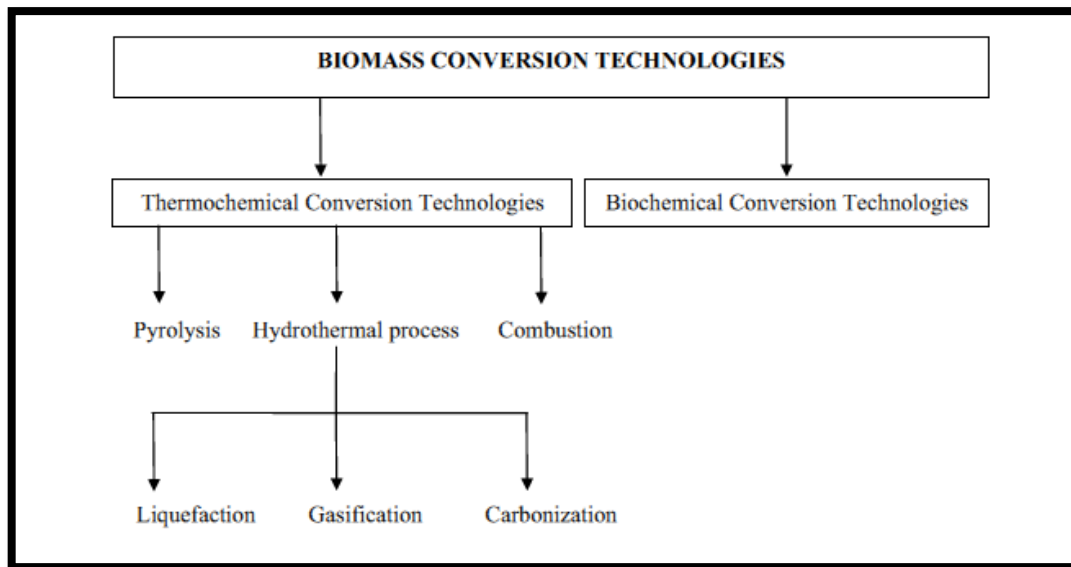


Figure 2-2 Biomass conversion technologies(Tekin et al., 2014)

The first group, biochemical conversion technologies, degrades biomass with enzymes and microorganisms. While, second group will convert biomass with thermochemical conversion technologies that degrades biomass with heat. The degradation of biomass by biochemical processes occurs naturally. These processes, which include aerobic and anaerobic degradation, fermentation, and enzymatic hydrolysis, are performed by bacterial enzymes and micro-organisms. The process in which yeast converts biomass into sugar and subsequently ethanol and other chemicals is called fermentation. It is used for commercial purposes and usually, a hydrolysis pre-treatment is used to convert cellulose and hemicellulose into sugar. Biomass can be directly used in combustion processes in order to obtain heat or to generate electricity. Products obtained from biomass gasification processes are generally used to generate heat or electricity in an engine or turbine. Solid and liquid products resulting from pyrolysis and liquefaction processes can be used as fuel after various improvements(Tekin et al., 2014).

The thermochemical conversion technologies can be subdivided into combustion, pyrolysis, liquefaction and gasification. The direct combustion is widely used on various scales to convert biomass energy to heat or electricity with the help of a steam cycle such as stoves, boilers and power plants. It is the main process that being adopted to utilize biomass energy. The energy produced through combustion process can be used to provide heat or steam for cooking, space heating and industrial processes. Large biomass power generation systems can have comparable efficiencies to those of

fossil fuel system, but the conversion process has a higher cost due to the moisture content of biomass. However, the economics can be significantly improved by using the biomass in combined heat and electricity production systems (Demirbas, 2001).

In the meantime, pyrolysis conversion process will convert biomass into liquid (bio-oil or bio-crude), charcoal and non-condensable gases, acetic acid, acetone and methanol by heating the biomass to about 750 K in the absence of air. It will produce energy fuels with high fuel-to-feed ratios, making it the most efficient process for biomass conversion and the method is the most capable of competing with and eventually replacing non-renewable fossil fuel resources. Through this process, the biomass will be heated in the absence of oxygen, or partially combusted in a limited oxygen supply. This will produce a hydrocarbon rich gas mixture, an oil-like liquid and a carbon rich solid residue.

For gasification conversion technology it is a form of pyrolysis, which is performed at high temperatures in order to optimize gas production. It is the latest generation of biomass energy conversion processes, and is being used to improve the efficiency and to reduce the investment cost of biomass electricity generation through the use of gas turbine technology. Conversion efficiency up to 50% can be achieved using combined cycle gas turbine systems, where waste gases from the gas turbine are recovered to produce steam for use in a steam turbine.

The ethanol could be produced from certain biomass materials which contain sugars, starch or cellulose with alcoholic fermentation conversion method. The best known source of ethanol is sugar cane, but other materials also can be used such as wheat and other cereals, sugar beet, Jerusalem artichoke and wood. Before undergoing the fermentation process the biomass needs to be converted into monomer sugars by using enzymatic hydrolysis process. Throughout this process, the biological degradation of the carbohydrates within the biomass is achieved using multiple enzymes in defined ratios to convert the carbohydrates to their monomer sugars (Van Dyk and Pletschke, 2012). Based on the study by Chu et al. (2012) they explored an integrated process of enzymatic hydrolysis and fermentation to enhance ethanol production from corn stover. Enzymatic hydrolysis at low substrate loading was carried out to obtain high hydrolysis yield, which avoids high viscosity and end product inhibition.

Pre-treatment of lignocellulose biomass is crucial for achieving effective hydrolysis of substrates as enzymatic hydrolysis of native lignocellulose produces less than 20% glucose from the cellulose fraction. Although pre-treatment is costly, the cost of hydrolysis will even larger without pre-treating removal or disruption of lignin has been established as essential for efficient bioconversion of lignocellulose to sugars. The removal can be achieved in several ways either through physical, chemical or enzymatic means. Removal of lignin by chemical means is achieved through pre-treatment of biomass by methods such as acid hydrolysis, steam treatment or alkaline treatment (Van Dyk and Pletschke, 2012).

2.3 *Sugar separation technology*

2.3.1 *High performance liquid chromatography (HPLC)*

High Performance Liquid Chromatography (HPLC) systems are commonly used technology to separate sugar such as monosaccharides, oligosaccharides, polysaccharides and neutral sugars in the industrial scale. There are different modes being used to separate sugars such as based on size exclusion, ligand conversion, partition, anion exchange and borate complex anion exchange.

Based on the previous study, one of the stationary phases used in liquid chromatography to separate sugar solution of xylose and glucose is silica-confined ionic liquid (IL) stationary phases (Bi et al., 2010). It is an efficient method for separation and determination of chemical compound. The stationary phases in liquid chromatography are used for separation of xylose and glucose includes those based on octadecylsilane and amino group as well as ion exchange resins. A typical separation media for ion-exchanged chromatography is sulfonated cross-linked styrene divinylbenzene cation exchange resin and it is the most applied in industrial separation. Silica-based columns still widely applied in small scale industries to separate sugar mixture with elution generally in order to increase the molecular weight. The disadvantage of the silica-based column is that it will gradually damage with the increase in water proportion. To overcome the weaknesses of the silica-based ionic liquid (IL) stationary phases were employed. It has been applied in many fields of analytical chemistry due to excellent chemical properties. It also had been synthesized and used as the stationary phases in high-performance liquid chromatography (HPLC) for separation of inorganic and organic compound (Bi et al., 2010).

2.3.2 Nanofiltration membrane (NF)

A cost-effective and easy maintenance method for the separation pentose sugar from hexose is by using nanofiltration (NF) membrane (Sjoman et al., 2007). The separation of uncharged substances is mostly based on the difference in molecular size and diffusivities. There is possibility for a partial separation of disaccharides (~300-360 g/mol) from monosaccharides (pentose and hexose, ~150-180 g/mol). Factors affecting the NF separation of saccharides, together with the membranes selectivity, are filtration pressure and temperature and total solution composition and concentration. An increase in pressure will lead to increased solvent flux and membrane compaction and these effects together will lead to an overall increase in retentions. While, for an increase in temperature from 25 to 60 °C was reported to decrease the retention due to reduced viscosity and increased diffusion. The size of a monosaccharide is equal or smaller than the cut-off sizes of NF membranes. The calculated diameters of the monosaccharide molecule approx. 0.6-0.8 nm and popular commercial NF are from 0.6-2.0 nm. Based on this study, NF has the possibilities to enhance the yield and partially replace chromatographic methods in xylose production. Sieving is the main separation mechanism with these small, uncharged and organic molecules. The retention of monosaccharides depend strongly on the permeate flux and higher retention were measured as permeate fluxes increased (Sjoman et al., 2007).

In addition, after researcher had found that it is possible to separate xylose and glucose with nanofiltration membrane, more advanced research had been made in order to improve the performance of membrane. Current research by (Mah et al., 2014) had study the ability membrane developed using interfacial polymerization reaction to separate xylose from glucose. Based on the characterization of the membrane developed, the average pore size of the membrane radius is 0.34 nm. Theoretically, xylose (Stoke radius = 0.325 nm and equivalent molar radius = 0.36 nm) can pass through the membrane and glucose (Stoke radius = 0.34 nm and equivalent molar radius = 0.36 nm) will be retained. Based on this study, increase in pressure will lead to decrease of separation performance which not in agreement with past studies and theory. The pressure difference used in this study was most likely too low for significant effect of pressure on NF to be seen. Decrease in xylose separation factor was observed at high xylose concentration in feed. This is probably caused by the concentration of polarization occurred that hindering the permeation of xylose.

2.4 Membrane technology

Membrane is a selective barrier between two phases. The membrane technology market is witnessing an era of rapid growth due to continuous research and development in both academia and private industry. Membrane technology has been applied for large variety of advance separation and purification processes, including biofuel production and purification. The advantages of membrane technology are it can minimize the capital cost, very flexible, provide compactness of the plant, have an optimal ratio between productivity and efficiency and also could save energy. Overall membrane separation basically depends on three basic principles: adsorption, sieving and electrostatic phenomenon. Figure 2-3 shows the schematic representation of the basic principle behind the membrane separation.

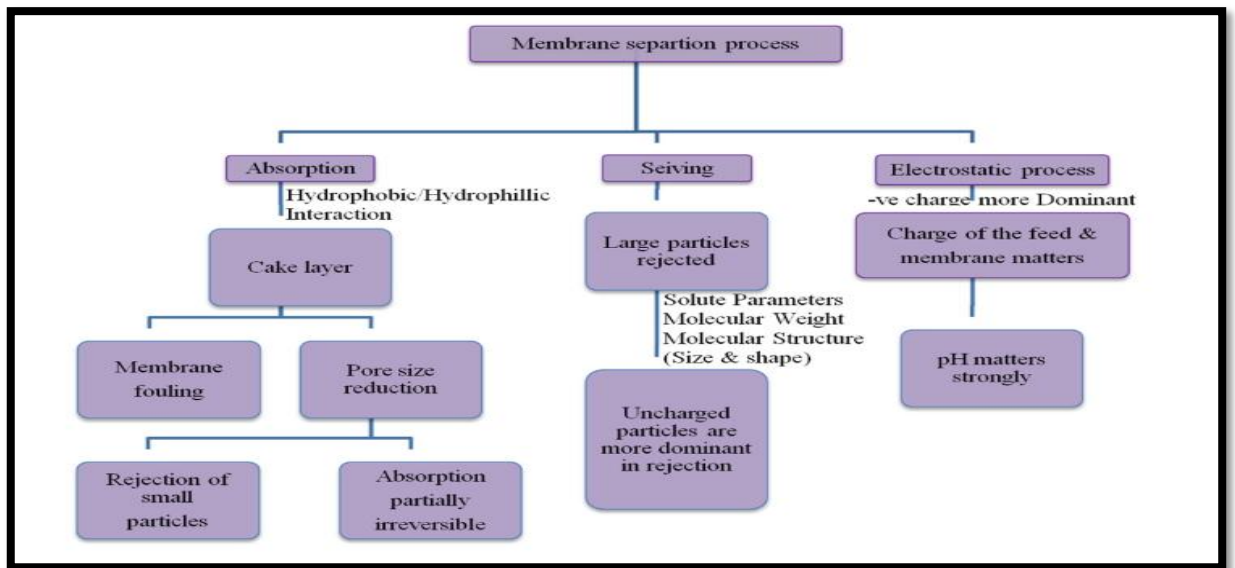


Figure 2-3 Schematic representing basic principles involved in membrane separation(Padaki et al., 2015).

2.4.1 Type of membrane

Figure 2-4 shows different type of membrane separation process together with the substance that can be separated by each process and also the membrane pore size.

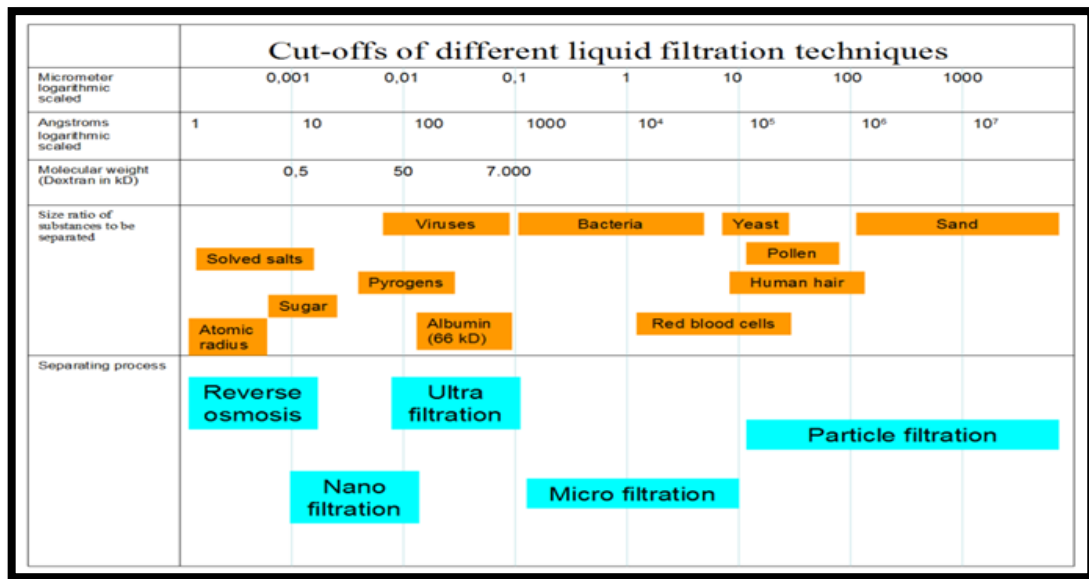


Figure 2-4 Cut-offs of different liquid filtration techniques

Ultrafiltration (UF) process is applied for the particles removal, microorganism and certain amount of dissolved organic matter. UF has been increasing used in the water treatment, separation and purification of different proteins. It has properties such as hydrophilicity, porous structure and antifouling nature that have a great influence on membrane performance (Nair et al., 2013) but to achieve high permeability, high surface porosity and good pore structure of membranes is very crucial (Yan et al., 2006). The weaknesses of UF process is, it is not being able to discriminate efficiently between the low molecular weight molecules

Whereas, for nanofiltration (NF) process it has gained their popularity once it was first introduced in the early 1980s because of their high selectivity for mono and multivalent ions, low operating pressures, and low operating cost compared to reverse osmosis (Liu et al., 2014). As an intermediate process between the UF and reverse osmosis (RO), the NF process offers a better rejection than UF. It had been widely used in various applications ranging from water treatment, pharmaceutical, oil and food industries.

RO is a high-efficient technique for dewatering process streams, concentrating or separating low-molecular-weight substance in solution, or cleaning wastewater. RO has the ability to concentrate all dissolved and suspended solids. The permeate will contain a very low concentration of dissolved solids. RO is commonly used for the desalination of seawater. RO is a pressure-driven process so no energy-intensive phase changes or

potentially expensive solvents or adsorbents are needed for RO separations (Williams, 2003).

Membranes are typically made of polymeric materials and inorganic (ceramic) materials. Polymer materials that were commonly used to prepare membrane are polysulfone (PSF), polyethersulfone (PES) and cellulose acetate (CA). Polymeric membranes offer some advantages including high efficiency to remove particles, low energy requirement and inexpensive compared with ceramic-based membranes. Polymeric blending approach has been extensively utilized for polymeric membrane fabrication due to its facile preparation procedure, versatility to incorporate desirable properties on the membrane, and also its profound ability to simultaneously modify the membrane properties during the phase inversion process. In order to enhance flux and antifouling property, hydrophilic additives such as hydrophilic polymers, amphiphilic copolymers and inorganic nanoparticles have been introduced (Padaki et al., 2015).

2.4.2 Membrane configuration

Membranes come in four basic configurations such as tubular, spiral, hollow fiber and flat sheet. Each configuration has their own unique characteristics to suit a wide range of process requirements. Flat sheet membrane has planar configuration and are mainly rectangular. They are used almost exclusively for membrane bioreactors for industrial and municipal application. Flat sheet usually being cast on solid backing materials and it has high surface area.

2.5 Nanofiltration membrane

Nanofiltration membrane process is a pressure-driven membrane separation technology in between reverse osmosis process and ultrafiltration membrane process. NF is termed as “Loose” reverse osmosis membrane. It operates at low pressure while reverse osmosis process need pressure >600 psi (Razdan and Shah, 2001). Organics >300 g/mol will be retained based on the cut-off solute with rejection above 92% because it is based on size and involves sieving effect. While ions rejection will be based on the size and valency. The average pore size diameter of NF is ~2nm and it is more porous compared to RO membrane and could cause concentration polarization and fouling but it can be overcome by having a better design and selecting material processing desirable properties (Razdan and Shah, 2001).

The nominal molecular weight cut off of a NF membrane is in the range 100-1000 Da. For mono and bivalent ions as well as organic compounds NF membrane will have good separation and high rejection for molecular weight from 100 to 500 Da (Han et al., 2014). Separation of solutes in the NF range is also dependent upon the micro-hydrodynamic and interfacial events occurring at the membrane surface and inside the membrane pore (Liu et al., 2014).

NF also has the ability of rejection low salt and high water flux at low pressure, separating low molecular weight organics from high molecular weight organics and passing solutions with high osmotic pressure at low pressure. With that ability, NF is an ideal membrane for water softening, desalting, food processing, waste-water treatment and for various separation processes in industry (Razdan and Shah, 2001).

NF is mainly fabricated via interfacial polymerization technique as it is a facile and fast method. The active layer can be attached onto various substrates. However, the substrate can be easily detached from the skin layer in harsh environment containing organic solvents such as ethanol because the compatibility between the support layer and the skin layer is so poor. Great effort had been made such as creating covalent linkage and constructive adhesive transition layer to enhance the strength between skin layer and the substrate surface (Lv et al., 2015).

Currently, most of commercially available membranes for NF are composite in nature; with a selective skin layer on the top of the porous substrate. There are several ways to construct the selective layer for NF membrane. Firstly, an active layer can be fabricated by integrally connecting it to the support layer. This method requires a delicate polymer dope formula and a precise control of casting conditions to avoid defect formation. Next, the selective layer can also be made based on the composite membrane concept that is the active layer and porous substrates are fabricated separately using different materials (Setiawan et al., 2011).

2.6 Effect of additives in nanofiltration

Flat sheet membrane will be prepared by the phase inversion technique. The crucial factor that need to be controlled during the membrane preparation are amount and type of polymers, types of solvent, type of additives mixed into the casting dope solution, coagulated bath temperature and type of coagulant bath (Feng et al., 2013). The effect of